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TABLE OF CONTENTS

		Page No.
I.	INTRODUCTION	1
II.	SECONDARY BATTERY ANODE	3
	A. Basic Electrochemical Experiments	4
	B. Pre-purification Procedures	11
	C. Properties of Cathodic Electrodeposits	13
	D. Summary	20
III.	SECONDARY BATTERY CATHODES	21
IV.	BERYLLIUM SYSTEMS	22
	A. Preparation of Organoberyllium Compounds	22
	B. Preparation of Beryllium Dialkyl Salts	22
	C. Summary	25

I. INTRODUCTION

The approaches of the various groups working in the field of high energy density batteries show important differences. While some groups are concentrating on the problems of increasing the electrolyte conductivity and developing chemically compatible high voltage couples, we have been more concerned with investigating the electrode processes occurring during the operation of a secondary battery with particular emphasis on understanding those factors limiting efficient utilization of electroactive material.

During the charge cycle of a secondary battery insoluble deposits are normally produced at both electrodes, a metal at the anode and a metal salt at the cathode. These deposits should be produced with 100% current efficiency since the concomitant process would normally be solvent decomposition often involving gassing. Likewise, the deposits should be dischargeable with 100% current efficiency. In our work we seek to develop electrode systems which display this behavior. In Phase II of this project, which we are now beginning, we expect to incorporate electrode systems in prototype cells, the operational behavior of which should give more clear-cut answers regarding the maximum energy density actually practicable in a secondary cell.

In a secondary battery cathode the maximum charge acceptance is directly limited by the amount of salt, the current density at which it is formed, the electrolyte composition, and the physical properties of the salt. The maximum useful charge acceptance is indirectly limited by the efficiency of subsequent discharge as a function of these parameters. The maximum charge acceptance for a secondary battery anode (the metal deposit) is primarily limited by the physical properties of the metal deposit, since a non-coherent, physically unstable deposit cannot be discharged with 100% efficiency. Current density and actual surface area are critical parameters in the efficient operation of a secondary battery. We intend to design electrodes with a knowledge of the role of these parameters in the electrochemical behavior of "ideal" flat, smooth electrodes, and to compare the operation of these electrodes with that of the ideal electrodes. The operation of prototype cells incorporating these electrodes should be more readily interpretable because of our more intimate knowledge of the electrode processes themselves, and a more direct assessment of the other variables affecting high energy density should then be more easily obtainable.

II. SECONDARY BATTERY ANODE

During this quarter we have concentrated on investigating the electrodeposition of lithium from propylene carbonate solutions of aluminum trichloride and lithium chloride and on studying the properties of the electrodeposits so obtained. Theoretically lithium should provide the highest energy density secondary battery anode. Since the observed behavior is reasonably close to that theoretically predicted we have not deemed it desirable at this time to devote more than cursory attention to other materials, aluminum, beryllium, etc.

Our first objective has been to deposit lithium with 100% current efficiency on flat, metal substrates. The quality of these deposits was assessed electrochemically by subsequent anodization, and also by chemical analysis. Certain basic electrochemical experiments, performed as described below, indicated that the efficient deposition of lithium should be more readily attainable than was in fact observed.

Theoretically, 100% deposition efficiency should be obtained if there is present in solution no species more readily reduced than the lithium ion, the deposition current does not exceed the limiting current for the reduction of the lithium ion, and if the deposit is adherent. The purpose of the basic electrochemical experiments described below was to determine the presence of species electro-reduceable before lithium and to determine the limiting current for lithium prior to further deposition studies.

A. Basic Electrochemical Experiments

The basic electrochemical experiments we have performed are quite familiar to electroanalysts. However, recognizing the wide divergence of interests in electrochemistry we feel it wise, for clarity, to precede our discussion of the results obtained with a brief summary of the principles of the method employed. Further reference may be had to any of a number of standard reference works on electroanalysis and electrochemistry.

All of our experiments have been performed in H-cells of standard construction incorporating a working electrode chamber of about 200 cm^3 connected through a fine porosity glass frit to an auxiliary electrode chamber of about 50 cm^3. Deaeration by argon or nitrogen was continuous through a coarse glass frit immersed in the body of solution or through a stream of gas played across the surface of the solution. Magnetic stirring was used for agitation of the solutions. Ambient temperatures was sufficiently constant to preclude the necessity for thermostating the solution for most measurements. Where greater temperature control was desired jacketed cells were used.

The auxiliary electrode was a platinum coil. The reference and working electrodes were constructed as follows: Small slices of metal rod, 5 to 7 mm in diameter, were soldered to copper wire and the whole imbedded in epoxy resin contained in a cylinder 1 to 1 1/2 inch in diameter and about one-half inch deep. The metal discs were so affixed as to present a flat, circular area flush with one face of the cylinder. In Figure 1 is shown a drawing of one such electrode. The entire surface was polished with fine emery paper. Occasionally polishing would be continued to a mirror finish with alumina, but this was merely for convenience in observing small amounts of film remaining on the electrode and no significant variations in electrode behavior were observed dependent on the degree of polish provided. The center disc was of silver and served as the reference electrode without further treatment. We found the potential of silver metal in the electrolytes used to be sufficiently constant to allow its use as a reference electrode. The potential deviated from the potential of the silver/silver chloride-electrode well within the desired accuracy of our potential measurements. The outer discs in the electrode shown in Figure 1 were the working electrodes.

Constant current was provided by one of several available Electronics Measurements electronically controlled constant current supplies (Model 630-C was most often used). A Wenking Potentiostat was used for potentiostatic measurements. The potential of the working versus the reference electrode was measured with an E-H Research Laboratories Model 230 electrometer, the signal of which was fed to a Varian G-14 recorder. Where switching was critical, mercury relay switches were employed. A more detailed description of the experimental set-up is contained in the First Quarterly Report, and significant changes have not been made since that time.

1. Polarography. Polarographic measurements are normally obtained by holding the potential of the working electrode constant until a steady state is attained, indicated by the constancy of the resultant current. A plot of steady state current versus potential constitutes a polarogram. In Figure 2 is shown a polarogram obtained in a solution initially 0.5 M in $AlCl_3$ and 0.079 M in LiCl. Such a polarogram was obtained by holding the working electrode potential constant with the Potentiostat and recording the current. The measurements were made in stirred solution. The current fluctuates about 5% about the average. At sufficiently high stirring rates the variation of current with stirring rate is not marked.

At about -.6 Volts reduction of a material, called species A in the Fifth and Sixth monthly reports, commences. At -1.4 Volts the limiting current for reduction of this species is reached; that is, the current is then limited by the rate at which species A can reach the electrode. The limiting current is generally directly proportional to concentration. At -3 Volts the reduction of lithium commences, indicated by the rise in current.

A limiting current for reduction of lithium could not be obtained in this manner since the time required for a steady state to be reached was attended with the formation of a lithium deposit, coarse and non-adherent, which was rather rapidly sloughed off the electrode, thus disturbing the steady state conditions required for attainment of a true limiting current.

It may be noted that, when not convenient to hold the potential of the working electrode constant, an essentially identical polarogram can be obtained by holding the current constant and measuring the steady state potential. This method has from time to time been employed when the operating limits of the potentiostat would have been exceeded.

Polarographic measurements may also be performed in quiet solution. In this case a longer time is required for a steady state to be reached and this steady state is less reproduceable, being more subject to convective effects arising from density and thermal gradients and vibrations affecting the electrolysis cell. We find that the steady state limiting current in quiet solution is about two-fifths the limiting current in stirred solution.

The polarogram shown in Figure 2 is typical of that obtained in propylene carbonate to which aluminum trichloride has been added. The magnitude of the limiting current shows significant variation from solution to solution. Attendant with the presence of the species indicated by the polarogram is the golden-brown color of the solution. A procedure of prepurification described below removes both the color and the polarographic limiting current. This species A, responsible for both the color and the limiting current, is reduceable before lithium and failure to remove the material from solution will prevent efficient deposition of lithium.

2. Chronopotentiometry. Chronopotentiometric measurements are non-steady state experiments performed in quiet solution at constant current. The potential of the working electrode is recorded as a function

of time. It is observed that, after a certain period of time, the "transition time", the potential exhibits a more or less abrupt jump. Theory predicts that the product of the current and the square root of the transition time, $i\ T^{1/2}$, is directly proportional to the concentration of species, the concentration polarization of which produces the potential jump, and to the electrode area.

In Figure 3 is shown a typical chronopotentiogram. This chronopotentiogram was obtained in a propylene carbonate solution, 0.5 M in $AlCl_3$ and 0.4 M in LiCl, at a current of 12 mA on copper electrode 0.34 cm^2. Since the product $iT^{1/2}$ is directly proportional to concentration and electrode area, the term, $iT^{1/2}/AC$ (Where A and C are the area) the concentration should be constant. We find this term for lithium to be 210 ± 10 mA $sec^{1/2}$ mM^{-1}cm.

Furthermore, since the product, $iT^{1/2}$ is proportional to concentration as is the polarographic limiting current, there should be a relationship between these two terms. We find the polarographic limiting current is about one-half of $iT^{1/2}$. As stated earlier the polarographic limiting current in quiet solution is about two-fifths that in stirred solution. Thus one calculates that the quiet solution steady state limiting current for lithium in propylene carbonate solutions containing aluminum trichloride should be given by:

$$i_{limiting} = (42)\ (A)\ (C)$$

Where i is in milliamperes, A in square centimeters, and C in moles per liter.

It was not possible to obtain reproduceable chronopotentiograms for the reduction of species A, whose presence was earlier deduced from polarographic measurements. The transition times obtained were normally significantly larger than those calculated from the relationship between polarographic limiting current and $iT^{1/2}$. We ascribe this deviation to adsorption of species A on the electrode surface, an effect quite often encountered in chronopotentiometric measurements.

Thus far we have concluded that there is initially present in solution a material, Species A, electro-reduceable before lithium, and which must be removed before efficient lithium deposition can be expected. The efficacy of removal of this species is indicated by the diminishment in the polarographic limiting current for this species. The limiting current for lithium deposition has been determined and electrolyses must be performed at currents below this limiting current for there to be efficient deposition. There remains the question of what occurs after lithium deposition -- that is, at currents above the limiting current for lithium, or after the transition time for lithium reduction. As discussed below in the section on the properties of the cathodic deposits we have found that aluminum metal appears to be deposited. However, we have not been able to obtain a well-defined chronopotentiogram for aluminum reduction in the presence of lithium chloride.

3. Expected Errors in Basic Electrochemical Measurements. In making polarographic and chronopotentiometric measurements and drawing certain conclusions therefrom we have neglected the important fact that, in the electrolytes employed, there is not an excess of supporting electrolyte. A theoretical analysis of the magnitude of the error expected due to the absence of supporting electrolyte has been recently undertaken by Dr. Per Bro of this laboratory. The results of his work indicate that, provided there is no great variation in the respective diffusion coefficients with concentration, the previously discussed proportionality between polarographic limiting current, chronopotentiometric $iT^{1/2}$, and concentration remain, even in the absence of supporting electrolyte. However, the magnitude of the constants employed in the various equations differ from those extant in the presence of supporting electrolyte. Since, in our work, we have been interested only in establishing the empirical relationship between limiting current, $iT^{1/2}$, and concentration we have not been further concerned with this problem.

A second source of error in the basic electrochemical measurements made concerns the measured potential between the reference and working electrodes. The reference electrode effectively probes a part of the total iR drop between the working and auxiliary electrodes. The magnitude of this iR drop may be several volts. A second iR drop is that which is developed across the diffusion layer when marked depletion of charged species exists in that region of solution. This may also be several volts. Nevertheless, our current concern is the obtaining of chronopotentiograms and polarograms which show successive transition times or successive limiting currents, denoting the initiation of new electrode reactions. Thus, although the voltage at which the polarographic or chronopotentiometric "breaks" occur may be in error by the iR drop, the general shapes of the polarograms or the chronopotentiograms are not significantly changed. For example, the chronopotentiogram shown in Figure 3 represents the reduction of lithium. The plateau at about -5 Volts followed by the rise in potential resulting from concentration polarization of lithium ion is about one volt above the reversible lithium potential. This is probably primarily ascribable to iR drop but does not negate the fact that the transition time observed is still a valid reflection of the concentration of lithium ion in solution.

B. Pre-purification Procedures

The presence of species A is deleterious for two reasons. It is reduced at potentials below that for lithium reduction, diminishing the current efficiency for this latter process, and it reacts chemically with the lithium, stripping it from the electrode surface. Two procedures for pre-purification have been used. In the first the propylene carbonate solution, containing aluminum trichloride, is allowed to stand in contact with metallic lithium or sodium for an extended period of time (several days).

There is a marked decrease in the golden-brown color of the solution but extensive electrochemical experiments have not been made to determine exactly how completely this procedure had resulted in the removal of species A.

The second pre-purification procedure involved the extended potentiostatic electrolysis of solutions. In this procedure a copper coil with an area of about 25 cm^2 was immersed in solution and maintained at a potential of -25V for twelve to fifteen hours. The current was recorded and the results are shown in Figure 4.

As a result of pre-electrolysis it was observed that the golden-brown color largely disappeared, the limiting current for species A was reduced to a fraction of its initial value, and the rate at which a lithium deposit was chemically stripped from the electrode was sharply reduced. The efficacy of electrolytic pre-treatment is thus clearly demonstrated. We believe that it is probable species A is a decomposition product resulting from the localized heating produced when aluminum trichloride is added to the propylene carbonate. It should be noted that the pre-purified solutions retain their characteristics after standing for several days under argon.

The current versus time plot shown in Figure 4 does not agree with that expected. Theory predicts that, when an electrolysis is performed at a potential such that the limiting current for the electrode process is maintained, then the current should decay exponentially with time as species producing this limiting current are removed from solution. This behavior is not evidenced by Figure 4. In fact, the observations made from Figure 4 suggest that two processes are occurring during potentiostatic pre-electrolysis. One process is the removal of species A at its limiting current, the other that of another species not at its limiting current. The second process would occur at a slower rate than the first. Thus, initially most of the current is used in exhausting the solution of species A; after this is nearly complete the observed current is largely that used in consumption of the second species. The effect is similar to that observed when measuring the radioactivity of a sample containing two radioisotopes of sufficiently different half lives. The experiments described in the next section suggest that aluminum is deposited concurrently with lithium, though in small amounts, and may even begin at potentials lower than for lithium deposition. It is possible, therefore, that this "second species" may be an aluminum species. It will be later shown that after an extended period of pre-electrolysis further potentiostatic pre-treatment effects no further change in the electrochemical properties of the solutions.

C. Properties of Cathodic Electrodeposits

Early in our work it was observed that lithium electrodeposited on a metal surface could not be re-oxidized anodically with 100% current efficiency. In Figure 5 are shown a set of results obtained in a propylene carbonate solution 0.5 M in $AlCl_3$ and 0.4 M in LiCl. The experiments from which the data shown in Figure 5 were obtained were performed by cathodizing a polished copper electrode in stirred solution at the current indicated and for a period of time corresponding to the number of millicoulombs given in the figure. After cessation of cathodization the deposit was anodized at 5 mA cm^{-2}. On anodization the potential remained constant at a potential slightly positive to the lithium open circuit potential of -3V. Completion of anodization was marked by a very sudden potential drop to the rest potential. The anodic current efficiency is given by the number of millicoulombs of anodic current passed divided by the number of millicoulombs of cathodic current originally applied.

Deposition of lithium on smooth electrodes is initially marked by the appearance of interference colors typical of thin films. The deposit then turns gray or black. The completion of anodization is marked by disappearance of the dark lithium deposit if the deposition had been performed at a sufficiently low current for a short enough period of time. In other cases a visible deposit remained on the electrode even after completion of anodization.

The limiting current for lithium in a solution 0.4 M in LiCl should be about 42 mA cm^{-2}. Since these solutions had been pre-electrolyzed one should expect 100% efficiency for lithium deposition at currents below 42 mA cm^{-2}. The failure to obtain 100% anodic current efficiency would seriously limit the energy density of such an electrode in a secondary battery. The trend observed in Figure 6 whereby the anodic current efficiency for a given number of cathodic millicoulombs is less the greater the current at which cathodization is effected was generally observed; no marked changes were observed between depositions performed at currents below the limiting current and currents above the limiting current other than a continuation of this general trend. Anodic current efficiency was also less the less concentrated the solution was in lithium chloride. For this reason we have not shown results obtained in these more dilute solutions.

From the results of the basic electrochemical experiments described above and the chemical analysis of the deposits described later we have concluded that it is possible to obtain close to 100% current efficiency for lithium deposition but that this deposit has a physical form such that it is impossible to completely re-oxidize the deposit anodically under the general conditions employed to date. We feel these results are extremely important in pointing to one critical area of research in which a good deal more work must be done for the development of a high energy density lithium secondary battery electrode.

A number of other metal surfaces were employed for lithium deposition. We found anodic current efficiency to be slightly less on a cobalt surface and significantly less on nickel and silver surfaces. Extensive measurements were not performed on these electrodes once preliminary work had indicated their inferiority to copper electrodes. In addition copper and silver electrodes were platinized by immersion in a platinic chloride solution and gold-plated by immersion in an auric chloride solution. The platinum or gold deposits were finely divided. No improvement in anodic current efficiency was noted on these electrode surfaces. Experiments have just begun on amalgamated copper electrodes and some improvement in anodic current efficiency has been observed but our results are yet too incomplete for inclusion in this report.

From the beginning of our work in the propylene carbonate solutions of aluminum and lithium chloride we had suspected that reduction of an aluminum species does occur. This is proved by chronopotentiometric experiments whereby a cathodic transition time occurs in solutions containing aluminum trichloride alone. The product, $iT^{1/2}$, is proportional to the concentration of aluminum in solution. No deposit forms however, and it appears likely that this reduction may not be that of the aluminum ion but of a molecule of solvent complexed with aluminum.

A series of experiments were performed in which a cathode deposit was formed under varying conditions and this deposit was then chemically analyzed. The principle of our procedure for chemical analysis was based on the fact that lithium reacts with water to yield a hydroxide ion which may be titrated to determine the total amount of lithium initially present in the deposit. In order for this titrimetric analysis to be sufficiently accurate a rather large amount of deposit must be formed, but the adherence of the deposit is not sufficiently good for one ever to obtain complete recovery of the lithium. Thus the method of analysis to be described is not an accurate measure of cathodic current efficiency but does serve to indicate the presence in the deposit of material other than lithium.

When aluminum is present in the deposit it also should react with water producing three hydroxide ions, which may also be titrated. Rather than titrate the hydroxide directly with standard acid our procedure consisted in washing the deposit into an excess of standard acid and back-titrating the excess with standard base. A typical experiment was one in which five copper electrodes, each about 0.34 cm^2 in area, were connected together, serving as the working electrode. A current of 25 mA was passed for 600 seconds in a stirred solution of propylene carbonate, 0.35 M in $AlCl_3$ and 0.15 M in LiCl. After completion of electrolysis the electrode was carefully removed from the solution and washed several times with fresh, vacuum distilled propylene carbonate to remove adsorbed electrolyte. A stream of water was then directed against the electrode into a small beaker containing five milliliters of 0.0493 M hydrochloric acid. The solution was diluted to about fifty milliliters with water and titrated with 0.0522 M sodium hydroxide using a glass electrode and pH meter. The resulting titration curve is shown in Figure 6.

Two breaks appear in the titration curve. The first break corresponds to complete consumption of the excess acid present -- that not reacted with the hydroxide produced by the reaction of lithium and aluminum with water. The number of milliequivalents total of lithium and aluminum on the electrode are calculated straight forwardly from the difference between the amount of acid initially present and the acid unconsumed. The second break in the titration curve corresponds to the reaction: $Al^{+3} + 3\,OH^{-} = Al\,(OH)_3$. And the amount of base required gives a direct measure of the amount of aluminum in the deposit.

This method of analysis was checked in several ways. First we were concerned that a sufficiently large amount of the aluminum-containing electrolyte might adhere to the electrode resulting in a large aluminum error on subsequent titration. We found this not to occur if the deposit is washed with propylene carbonate. The error is substantial if the deposit is washed with n-hexane.

The validity of using the second break in the titration curve for determining the amount of aluminum was assessed by performing the same titration on aliquots of a standard solution of aluminum trichloride. The results agreed within two percent of those expected. Further, an aliquot of the aluminum trichloride containing propylene carbonate electrolyte was added to excess acid and titrated with standard base; the amount of aluminum thus determined agreed with the concentration of aluminum trichloride in the electrolyte to within a few percent. A further check on the procedure was performed by titrating a solution of the dissolved deposit to the first end point and then adding excess disodium dihydrogen EDTA. Aluminum ion strongly complexes with this material releasing two hydrogen ions which are titratable with standard base. The amount of aluminum calculated from the results of this titration agreed with those obtained by direct titration of the aluminum ion with standard base.

In Figure 7 are shown results obtained for chemical analysis of deposits obtained in propylene carbonate solution, 0.35 M in $AlCl_3$ and 0.15 M in LiCl. These results exhibit the general pattern observed in a number of such experiments. All depositions were made on five interconnected copper electrodes, each about 0.35 cm^2. A total of 15,000 millicoulombs of cathodic current were applied for each run, this giving a convenient titer during subsequent analysis. The limiting current for lithium reduction in these solutions is about 15 mA cm^{-2}. Thus one sees that a very significant amount of aluminum codeposition occurs even at currents well below the lithium limiting current.

The physical appearance and adherence of the deposit varies widely depending on the conditions of electrodeposition. There appear to be three general types of deposit. The first is that formed at low currents, less than half of the limiting current. This deposit is gray and quite adherent. At currents near the theoretical limiting current the deposit is black and finely dendritic. This deposit is, not unexpectedly, quite inadherent.

At currents such that the amount of aluminum codeposited is large (e.g. 30-40%) the deposit is rather matte-like and quite adherent. Considerably more work must be done before a clear picture of the inter-relationship of current density, electrolyte composition, and deposit adherence is obtained. The results reported should therefore be considered not conclusive but indicative of areas in which more fruitful research may be done. A noticeable improvement in adherence was observed when depositions were done on an amalgamated copper surface.

D. Summary

We conclude that on cathodization of a propylene carbonate solution containing both lithium chloride and aluminum trichloride 100% current efficiency is obtainable but that the deposits do contain significant amounts of aluminum. The adherence of these deposits is sensitive to the deposition current and the electrolyte concentration. The physical form of the deposits is such that it is impossible to obtain good anodic current efficiency for re-oxidation for other than very thin deposits.

Our future work in the development of a useful secondary battery lithium anode will be directed towards finding those conditions under which electrodeposition of a deposit with satisfactory electrochemical properties can be obtained. Other electrolytes (especially acetonitrile and dimethylformamide) will be investigated and other electrodes will be used. Work has begun on the preparation of porous copper electrodes and amalgam electrodes.

III. SECONDARY BATTERY CATHODES

Thus far we have found that only silver can be anodized to an insoluble salt with 100% current efficiency in the propylene carbonate electrolytes. The salt formed can be cathodically stripped with excellent current efficiency without excessive polarization. However, silver is a less desirable system because of its high atomic weight and one seeks other systems. Thus far we have found that iron, cobalt, and nickel do not appear to form insoluble salts on anodization. Furthermore, the reduction of the material formed on anodization is reduced with sufficiently large overvoltages as to negate any superiority to silver salt electrodes.

Electrolytes have been prepared in which fluoride has been added to the system. One electrolyte employed aluminum trichloride and sodium fluoride, the other electrolyte employed potassium hexafluorophosphate alone. In neither system was any marked change observed in the anodic behavior of iron, cobalt, or nickel.

Anodization of copper electrodes in propylene carbonate containing aluminum trichloride and lithium chloride produces a film which can be reduced with about 50 - 75% efficiency before polarization occurs. The film appears to be slowly soluble. Experiments have only recently begun on copper electrodes and we shall delay a presentation of our results until the next monthly report.

IV. BERYLLIUM SYSTEMS

A. Preparation of Organoberyllium Compounds

The techniques for synthesizing dialkyl and diaryl beryllium compounds have been refined to the point where consistent yields in excess of 50% can be achieved. At least 0.2 moles each of diethylberyllium, di-n-propylberyllium, diisopropylberyllium, and diphenylberyllium were prepared and used in complex salt formation studies.

A modification of the method for making diethylberyllium was evolved which offers the advantages of greater simplicity and minimum exposure of reactants. It consists of a one-step process in which an ether solution of ethyl bromide is added dropwise to a stirred mixture of magnesium turnings in a solution of beryllium chloride in ether. Thus the Grignard reagent reacts as rapidly as it is formed and the ether solution of diethylberyllium can be filtered off directly for distillation. Yields are comparable to the usual two-step procedure.

An attempt was made to prepare diphenylberyllium by adding phenyllithium solution to beryllium chloride etherate. When stoichiometric quantities of reactants were used, the only product that could be isolated was a pale yellow crystalline solid which was determined to be the beryllium chloride-diphenylberyllium complex salt.

B. Preparation of Beryllium Dialkyl Salts

Following the successful preparation of various dialkylberyllium compounds a study of their ability to form complex halide salts was undertaken.

The procedure used was essentially the same in all cases. About 1 gram of the selected halide was mixed with 10 milliliters of the dialkylberyllium distillate in an argon filled dry box. The mixture was stirred and heated to boil off any liberated ether. The residue was then washed several times with heptane to remove any unreacted dialkylberyllium. The residue was then vacuum dried at moderate temperatures to remove the remaining heptane. The results are summarized in Table I.

1. Dimethylberyllium. Although beryllium chloride dissolved in an ether solution of dimethyl beryllium, no heat or gas evolution occurred. Evaporation of the ether gave a mixture of unchanged starting materials. Beryllium fluoride was not soluble under the same conditions indicating no reaction.

2. Diethylberyllium. Many attempts to prepare a complex salt with potassium cyanide gave only unreactive infusible white powders rather than the low melting crystals reported in the literature. The potassium cyanide used was anhydrous reagent grade. The reason for failure to obtain the anticipated product has not been ascertained and further work is indicated.

Tetraethylammonium chloride reacts vigorously with evolution of heat and gas. The gummy solid product obtained, although very reactive, contained beryllium oxide and could not be used for conductivity measurements.

Beryllium chloride also reacted with heat and gas evolution. The product was a pale yellow liquid having a specific conductivity of 1.60×10^{-4} ohm^{-1} cm^{-1}.

3. Di-n-propylberyllium. Sodium fluoride and tetramethylammonium bromide gave complex salts which were white powdery solids having no melting points.

Beryllium chloride gave a viscous brown liquid complex which had a resistivity beyond the range of the measuring equipment. It gradually solidified on storage in the dry box.

4. Diisopropylberyllium. Both beryllium chloride and tetraethylammonium chloride gave white solid complex salts which were not investigated further.

5. Diphenylberyllium. The yellow solid complex of diphenylberyllium and beryllium chloride obtained from the reaction of beryllium chloride and phenyllithium was found to be soluble in propylene carbonate. A solution approximately 20% by weight had a specific conductivity of 1.30×10^{-4} ohm^{-1} cm^{-1}.

Thus of all the combinations studied only beryllium chloride and diethylberyllium gives a definite liquid complex salt. While the specific conductivity does not approach that of a fused salt, it is sufficiently high to merit further investigations of larger quantities of this material. Further work in two areas of immediate interest is indicated. First we are interested in the use of liquid beryllium chloride - diethylberyllium complex salts as a solvent for compatible ionic salts, particularly lithium chloride. Secondly, we are planning a chronopotentiometric study of the beryllium metal electrode in the complex salt electrolyte. The feasibility of this hinges on the resolution of the many difficulties attendant to the handling of larger quantities of such reactive material.

C. Summary

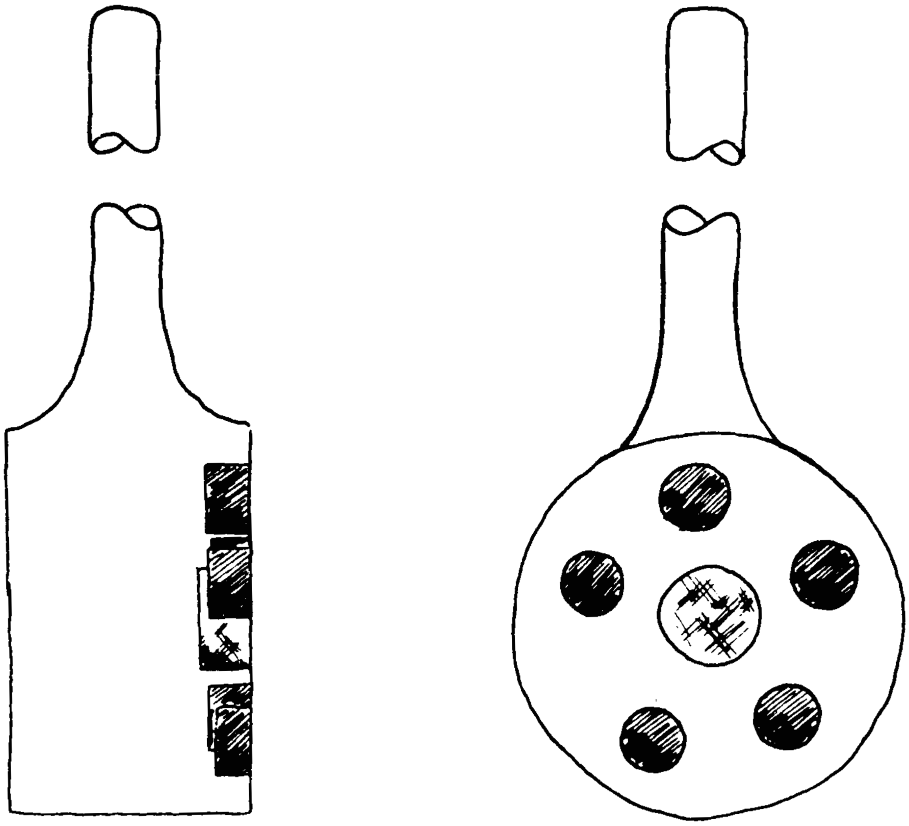
Successful procedures for the synthesis of dialkylberyllium compounds have been worked out. Diethyl, di-n-propyl, diisopropyl, and diphenylberyllium were prepared. A variety of dialkylberyllium - tetraalkylammonium or metal halide complex salts were prepared. Of these only beryllium chloride gives a product liquid at room temperature. The beryllium chloride - diethylberyllium complex had a specific conductivity of 1.6×10^{-4} $\text{ohm}^{-1}\ \text{cm}^{-1}$ whereas the beryllium chloride - di-n-propylberyllium complex had a conductivity too low to measure.

TABLE I

Organoberyllium Complex Salts

	Dimethyl-beryllium	Diethyl-beryllium	Di-n-propyl-beryllium	Diisopropyl-beryllium	Diphenyl-beryllium
Potassium Cyanide		White Powder			
Beryllium Chloride	No Reaction	Yellow Liquid	Viscous Brown Liquid	White Powder	Yellow Solid
Beryllium Fluoride	No Reaction				
Sodium Fluoride			White Powder		*No Reaction
Tetraethyl-ammonium chloride		Gummy White Solid		White Powder	*No Reaction
Tetramethyl-ammonium bromide					

*The diphenylberyllium used was later found to be the beryllium chloride complex salt of diphenylberyllium



SIDE VIEW FRONT VIEW

FIGURE 1

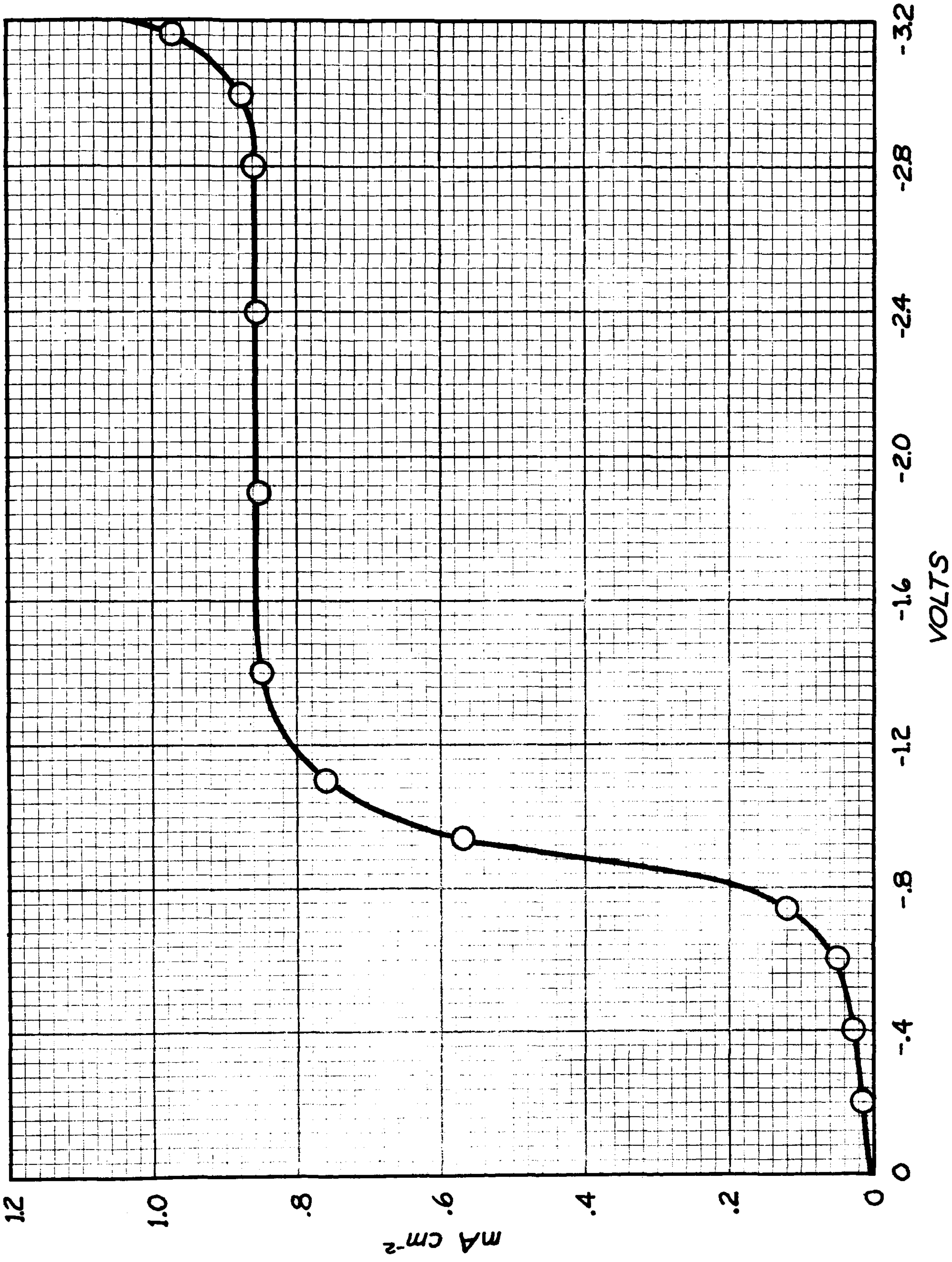


FIGURE 2.

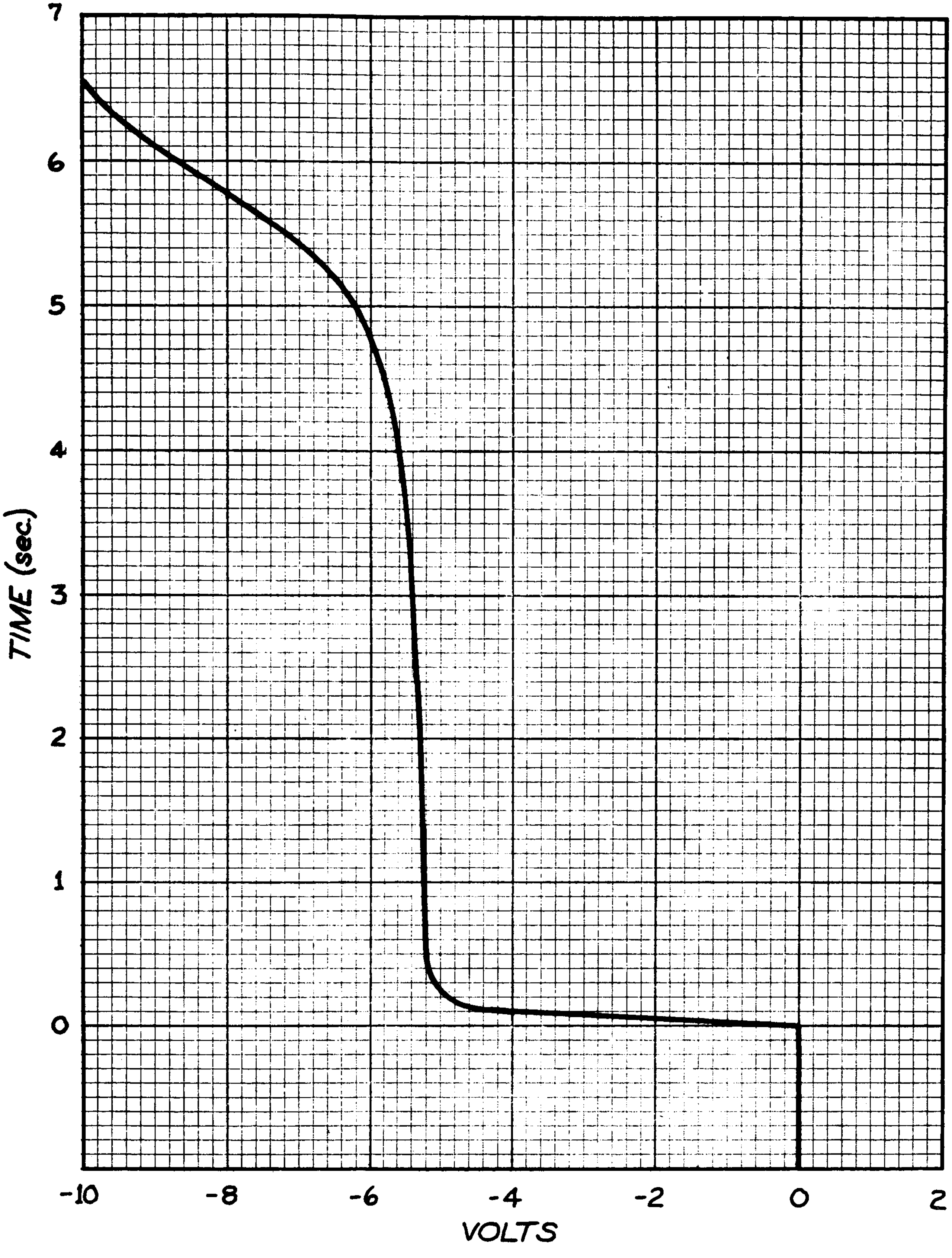


FIGURE 3.

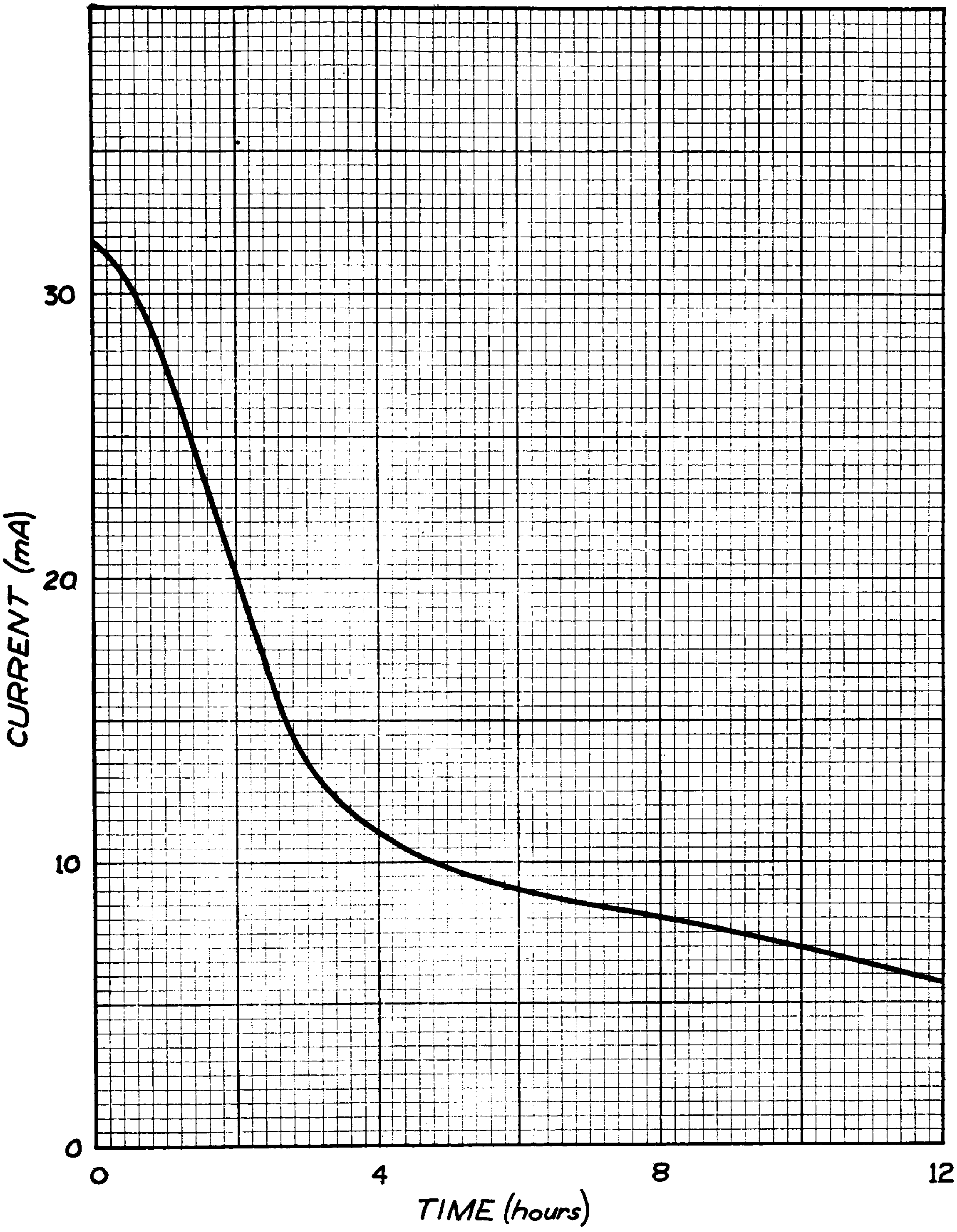


FIGURE 4.

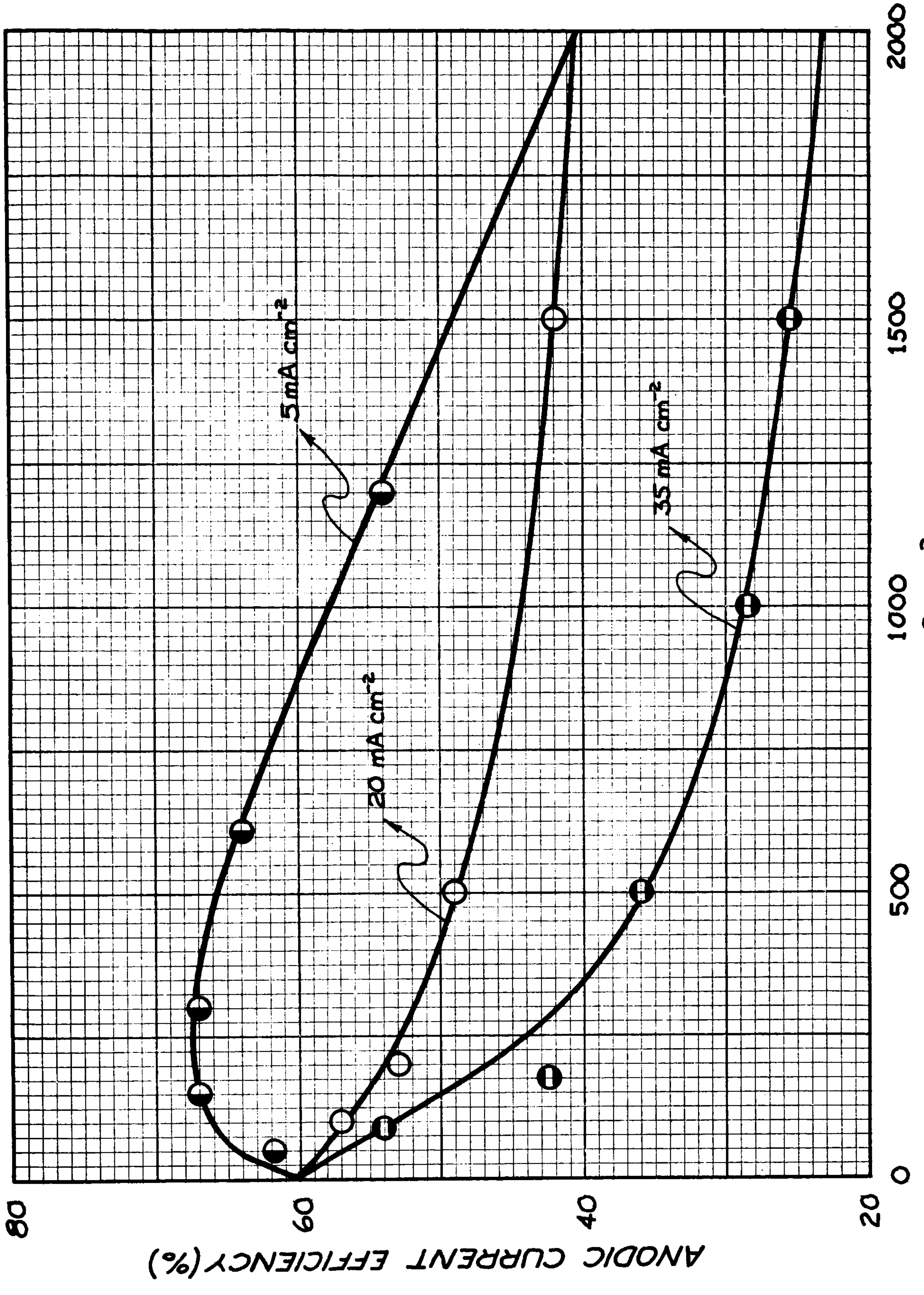

80
60
40
20
ANODIC CURRENT EFFICIENCY (%)
0
500
1000
1500
2000
mC cm^{-2}
5 mA cm^{-2}
20 mA cm^{-2}
35 mA cm^{-2}

FIGURE 5.

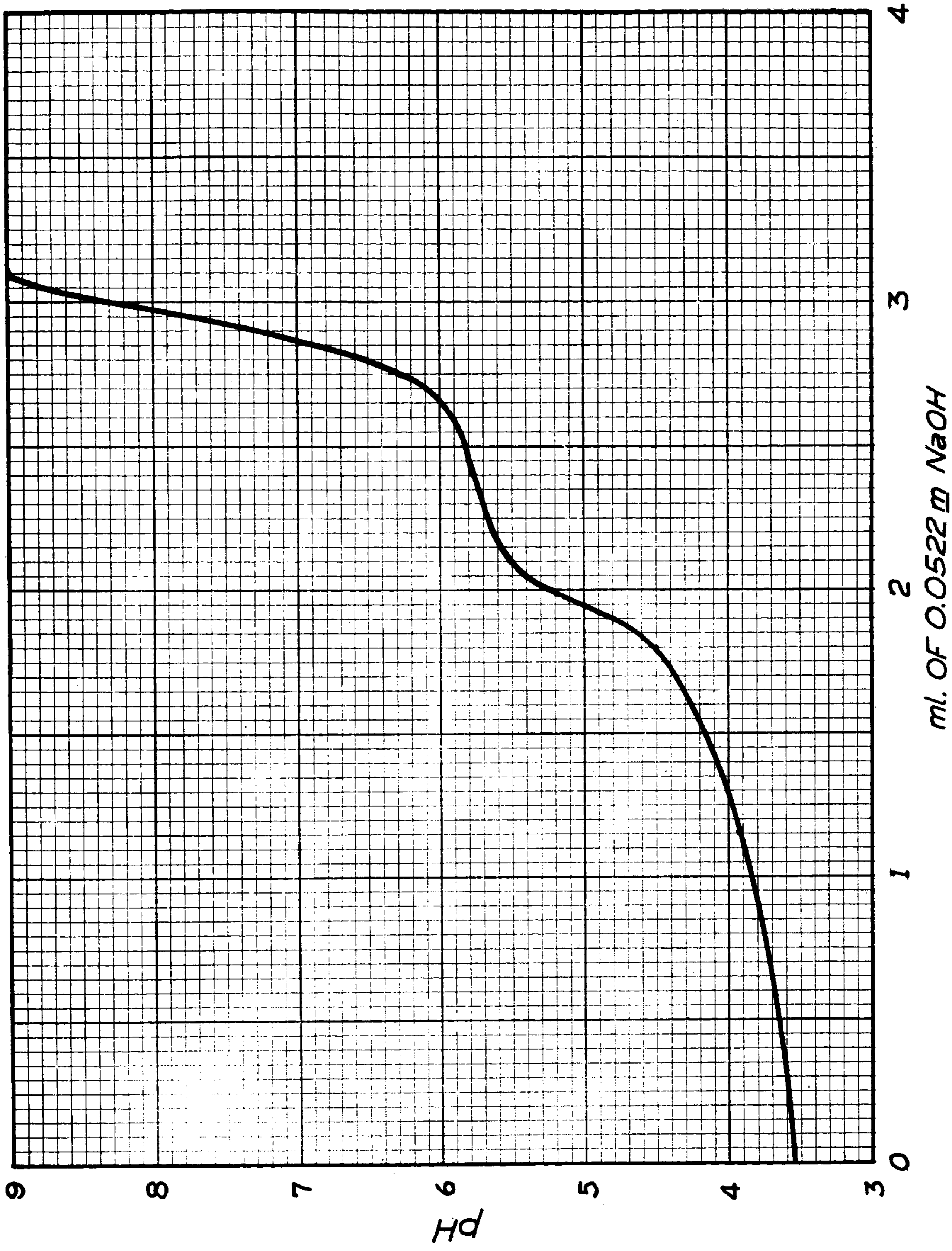


FIGURE 6.

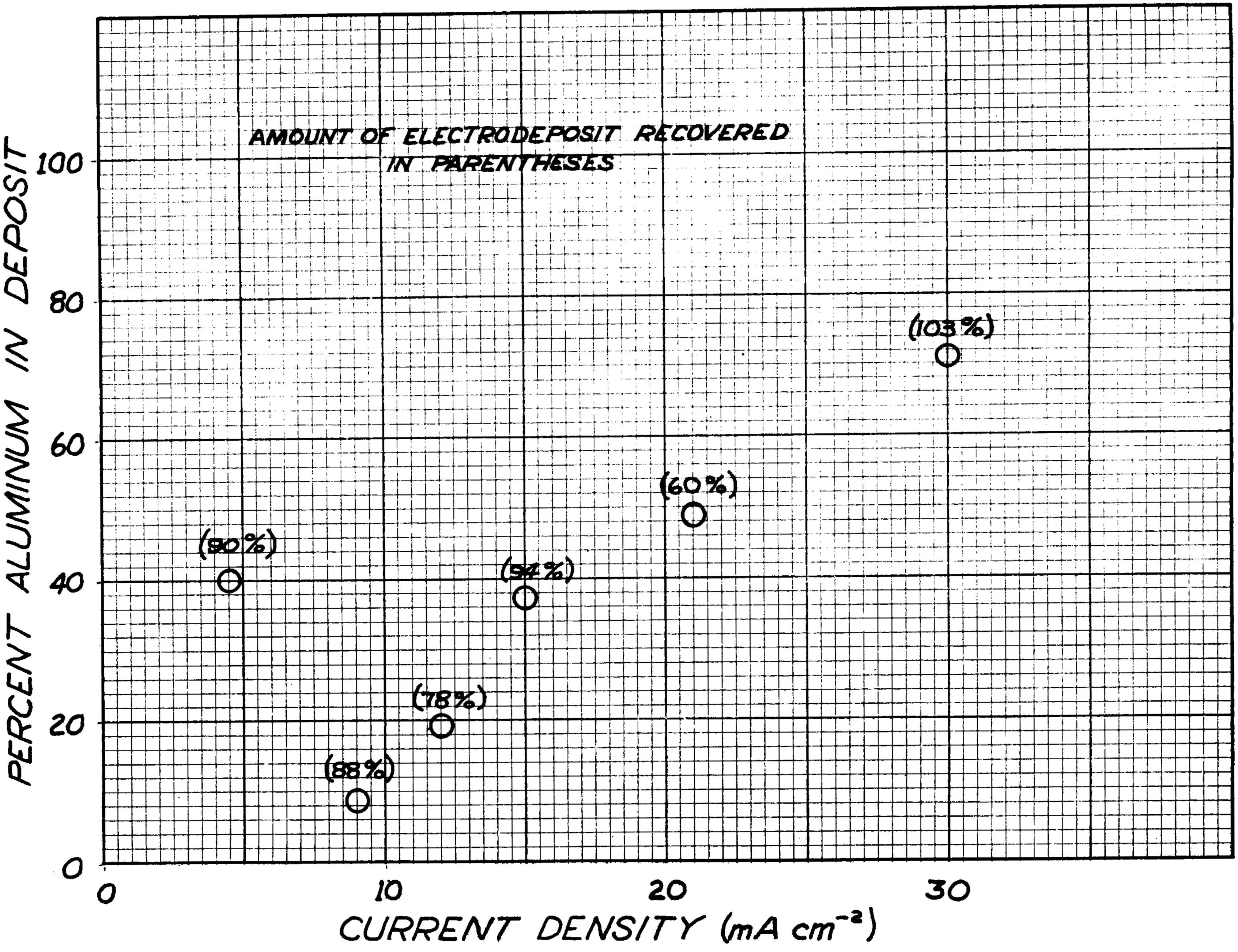

AMOUNT OF ELECTRODEPOSIT RECOVERED
IN PARENTHESES
(90%)
(88%)
(78%)
(94%)
(60%)
(103%)
PERCENT ALUMINUM IN DEPOSIT
0
20
40
60
80
100
0
10
20
30
CURRENT DENSITY (mA cm^{-2})

FIGURE 7.